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LOW ENERGY ATOMIC COLLISIONS

**Final Scientific Report
for Period 1 July 1973 - 30 September 1977**

Contract Number: F44620-74-C-0002

**Principal Investigator: Dr. R. H. Neynaber,
565-7171, Ext. 365**

AFOSR Project Monitor: Dr. Ralph E. Kelley

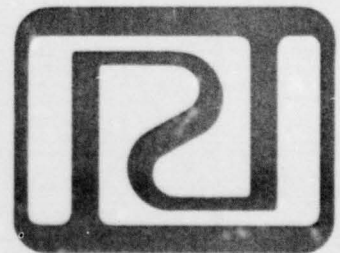
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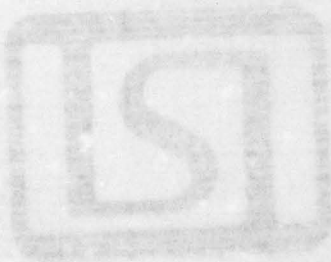
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AFSC Project Monitor: Dr. Ralph E. Kelley

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The goal of this experimental program was to study selected chemi-ionization and ion-molecule reactions to better understand the dynamics of such collisions and to provide data to assist in the formulation of theory. The relative energy of the reactants for these studies was varied from threshold to 10 or 20 eV. Both crossed and merging-beams techniques were used.

These studies give a clearer picture of the role played by the kinetic and internal energy of reactants at low relative energies. This is important for the development of advanced Air Force systems that require communication through either a naturally or artificially ionized atmosphere and for the development of propulsion systems for the Air Force.

ACCOMPLISHMENTS

This section will be devoted to describing unique techniques that we have developed during this contract for studying chemi-ionization and ion-molecule reactions. In addition, from the data we obtained using these techniques, we will attempt to make fairly general observations of the dynamics, cross sections, branching ratios, etc., for these reactions. In general, specific details of reactions studied will not be presented. These are available in the published papers listed in the following section.

1. We have perfected a merging-beams technique for measuring Penning ionization (PI) cross sections which employs a retarding potential device as well as an electrostatic hemispherical analyzer.
2. (a) We have developed (although not fully) a method for determining well-depths of potential curves for two reactants which can undergo PI, i.e., $A^* + B \rightarrow A + B^* + e$. In particular, the techniques can be used for a so-called attractive system. An attractive system is defined as one for which $W/\epsilon^* \ll 1$, where W is the relative kinetic energy of the reactants A^* and B and is in the thermal energy range, and ϵ^* is the well depth of the potential curve $V^*(R)$ of the reactants. The method depends upon measuring the intensity of the Penning ions versus W' , the relative energy of the heavy products of the PI reaction. Then $W'_M - W \approx \epsilon^*$, where W'_M is the W' for maximum intensity.

Well depths have been obtained by other experimentalists using the technique of Penning Electron Spectroscopy.

(b) For repulsive systems, i.e., $W/\epsilon^* \gg 1$, we have found that $W_M' - W \approx 0$. This is consistent with the two-state potential curve model, which has been used successfully in explaining experimental data for associative ionization (AI) and PI.¹

3. (a) We have developed a merging-beams technique for studying chemi-ionization between two metastable reactants. For rare gas reactants this technique employs two charge-transfer cells containing alkali vapor. Rare-gas ion beams are neutralized and rendered partially metastable in these cells.

(b) Our study of the reaction $\text{He}^* + \text{Ne}^* \rightarrow \text{HeNe}^+ + e$ using the technique mentioned above represents the first direct evidence of AI for which both reactants are excited.²

4. (a) We have found that relative cross-section curves Q_{AI} versus W for attractive systems which undergo AI, i.e., $A^* + B \rightarrow AB^+ + e$, are similar. Although the shape of a particular curve gradually changes, roughly $Q_{\text{AI}} \propto W^{-1}$. Systems that we have studied which are apparently attractive and have this rough dependence include $\text{He}^* - \text{D}$, $\text{He}^* - \text{H}$, $\text{He}^* - \text{N}$, $\text{He}^* - \text{Ne}$, and $\text{Ar}^* - \text{Na}$. This observed "universal" relative cross-section curve should prove a useful test for any theoretical treatment of AI for attractive systems. For such systems it appears that a satisfactory theory must result in such a curve.

(b) Repulsive systems that we have studied are $\text{Ne}^* - \text{Ar}$ and $\text{Ne}^* - \text{Kr}$. Their relative Q_{AI} curves are identical and quite different from those for attractive systems. In particular, $Q_{\text{AI}} \propto W^{-1/2}$ for $W < 0.1$ eV, and $\propto W^{-2}$ for $W > 0.1$ eV.

5. According to the two-state potential curve model,¹ the total ionization cross section Q_{T} (where $Q_{\text{T}} \equiv Q_{\text{AI}} + Q_{\text{PI}}$) $\propto W^{-1/3}$ for attractive systems which are controlled by van der Waals

forces. We have shown that several attractive systems we have studied are apparently controlled by van der Waals forces at low W . These include Ar^*-Na and He^*-Ne^* .

6. All of the PI reactions we have studied are directed with the Penning ion scattering predominantly along the direction of the parent neutral. A small fraction of the scattering occurs at all angles to this direction. It would seem reasonable to suggest that PI is always directed.
7. Branching ratios R (where $R \equiv Q_{\text{AI}}/Q_{\text{T}}$) for attractive systems, especially for two metastable reactants, tend to be small (a few percent or less) at thermal energy. For example, at $W = 0.033$ eV, $R = 0.0033$ for He^*-Ne^* ; whereas, for Ne^*-Ar , $R = 0.21$. For Ar^*-Na (which is like two metastable reactants since Na is similar to Ne^*), $R = 0.071$.
8. (a) A molecular-beam technique has been developed for measuring the previously unknown composition of rare-gas beams consisting of metastable and ground-state atoms generated by the rather common method of charge transfer of rare-gas ions in an alkali vapor. The technique depends upon finding an ion-neutral reaction which proceeds for ground-state rare-gas atoms but not for metastables. The composition can then be determined by comparing the product ion current resulting from this reaction when the rare-gas reactant beam is the composite of metastable and ground-state atoms with the current when the rare-gas reactant beam is entirely in the ground state. The method has been used to determine the composition of partially metastable beams of He, Ne, and Ar, and presumably would also work for beams of Kr and Xe.

(b) The composition of partially metastable rare gas beams has been calculated using a method of statistical weights. There is fair agreement with experimental results obtained by the method described above.

PAPERS AND TALKS

Published Papers

1. G. D. Magnuson and R. H. Neynaber, "Associative Ionization in Collisions of Metastable Helium with H and D," J. Chem. Phys. 60, 3385 (1974).
2. a) J. A. Rutherford and D. A. Vroom, "Charge Transfer Cross Sections for Metastable $N^+(^1D)$ in Collision with Krypton and Carbon Monoxide," J. Chem. Phys. 62, 1460 (1975); (b) J. A. Rutherford and D. A. Vroom, Erratum: "Charge Transfer Cross Sections for Metastable $N^+(^1D)$ in Collision with Krypton and Carbon Monoxide" [J. Chem. Phys. 62, 1460 (1975)], J. Chem. Phys. 65, 1603 (1976).
3. R. H. Neynaber and G. D. Magnuson, "Chemi-ionization in Collisions of Metastable Neon with Argon," Phys. Rev. A11, 865 (1975).
4. R. H. Neynaber and G. D. Magnuson, "Penning Ionization of D by He Metastables," J. Chem. Phys. 62, 4953 (1975).
5. R. H. Neynaber and G. D. Magnuson, "Associative Ionization in Collisions Between Two Excited Reactants," Phys. Rev. A12, 891 (1975).
6. J. A. Rutherford and D. A. Vroom, "Ion-Molecule Reactions of N^+ and O^+ with Nitric Oxide," J. Chem. Phys. 64, 1251 (1976).
7. R. H. Neynaber and G. D. Magnuson, "Penning and Associative Ionization in the Metastable Neon-Krypton System," Phys. Rev. A14, 961 (1976).
8. R. H. Neynaber and G. D. Magnuson, "Composition of Partially Metastable Rare Gas Beams," J. Chem. Phys. 65, 5239 (1976).
9. R. H. Neynaber and G. D. Magnuson, "Chemi-ionization in Collisions of Metastable Argon with Sodium," J. Chem. Phys. 67, 430 (1977).

Manuscript Submitted for Publication

1. R. H. Neynaber and S. Y. Tang, "Chemi-ionization in Collisions of Metastable Helium with Metastable Neon," to be published in December 15 issue of J. Chem. Phys.

Prepared Talks

1. R. H. Neynaber and G. D. Magnuson, "Chemi-ionization in Collisions of Metastable Ne with Ar," Twenty-Seventh Annual Gaseous Electronics Conference, Houston, Texas, October 22-25, 1974.

2. R. H. Neynaber and G. D. Magnuson, "Associative Ionization in Collisions Between Metastable Helium and Metastable Neon," IX International Conference on the Physics of Electronic and Atomic Collisions, University of Washington, Seattle, Washington, July 24-30, 1975.
3. R. H. Neynaber, "Merging-Beams Studies of Chemi-ionization," AFOSR Contractor's Meeting, AFWL, Albuquerque, New Mexico, April 12-17, 1976.
4. R. H. Neynaber and G. D. Magnuson, "Penning and Associative Ionization in the Ar*-Na System," X International Conference on the Physics of Electronics and Atomic Collisions, Paris, July 21-27, 1977.

PERSONNEL

The following scientists have participated in the research of this contract: R. H. Neynaber, S. Y. Tang, G. D. Magnuson, S. M. Trujillo, J. K. Layton, J. A. Rutherford, and D. A. Vroom.

USE OF RESULTS

For Review Papers

The subject of chemi-ionization is of much interest lately. An understanding of chemi-ionization reactions is important for the further development of many areas including laser technology, combustion, high voltage switching, and commercial and residential lighting.

Several review articles on the subject or associated with it are planned for the near future. Some of the authors of these articles who have asked to use our results are listed below.

1. H. Hotop and A. Niehaus, "Penning Ionization," to be submitted to Review of Modern Physics.
2. J. N. Bardsley, an article on resonant states of atoms and molecules which will include a discussion of Penning and associative ionization processes, to be submitted to Review of Modern Physics.
3. R. S. Berry, "Attachment and Detachment Processes," Advances in Electronics and Electron Physics (1978).
4. A. C. H. Smith, an article on chemi-ionization, to be submitted to a foreign journal.

By Other Experimentalists and Theoreticians in the Field

Our results are being used by experimentalists and theoreticians who are also engaged in research directed at understanding the dynamics of atomic and molecular collisions. These scientists include Prof. R. S. Berry (Dept. of Chem., Univ. of Chicago), Prof. W. A. Chupka (Dept. of Chem., Yale Univ.), Prof. J. L. Franklin (Dept. of Chem., Rice Univ.), Dr. A. P. Hickman (SRI International), Prof. W. H. Miller (Dept. of Chem., Univ. of Calif. at Berkeley), Prof. J. C. Polanyi (Dept. of Chem., Univ. of Toronto), and Prof. G. K. Walters (Dept. of Physics, Rice Univ.).

By Industry

As an example of the use of our results by industry, we are aware IBM is interested in chemi-ionization rates for the development of gas display discharge devices. Such devices are part of a growing field in computer and electronic technology. These display discharges take place in isolated high pressure (>100 torr) Penning mixtures (e.g., Ne + 0.1% Ar) confined within a narrow gap ($\sim 10^{-2}$ cm) formed at the intersection of orthogonal metal line conductors covered by insulator surfaces. These devices can be used to show numbers and other characters and act as a link between the operations of an electronic system and a human operator.

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1. See, for example, (a) A. Niehaus, Ber. Bunsenges Phys. Chem. 77, 632 (1973); (b) H. Hotop, Radiation Res. 59, 379 (1974); (c) E. Illenberger and A. Niehaus, Z. Physik B20, 33 (1975).
2. See, for example, the following reviews of chemi-ionization: (a) A. Fontijn, Prog. React. Kinet. 6, 75 (1972); (b) A. Fontijn, Pure Appl. Chem. 39, 287 (1974).